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(REV 5-93)

US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY DOCKET NUMBER
2001_1848A

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371

U.S. APPLICATION NO.
(if known, 37 CFR 1.5)
NEW 10/019431

International Application No.	**International Filing Date**	**Priority Date Claimed**
PCT/NO99/00324	October 25, 1999	July 2, 1999

Title of Invention
CORROSION RESISTANT Mg BASED ALLOY CONTAINING Al, Si, Mn and RE METALS

Applicant(s) For DO/EO/US
Ketil PETTERSEN, Marianne VIDEM and Jan Ivar SKAR

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a FIRST submission of items concerning a filing under 35 U.S.C. §371.

2. [] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371.

3. [X] This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).

4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. [X] A copy of the International Application as filed (35 U.S.C. §371(c)(2)) (in English)
   a. [] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [X] has been transmitted by the International Bureau.
   c. [] is not required, as the application was filed in the United States Receiving Office (RO/US)

6. [] A translation of the International Application into English (35 U.S.C. §371(c)(2)).

7. [] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)).
   a. [] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [] have been transmitted by the International Bureau.
   c. [] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [] have not been made and will not be made.

8. [] A translation of the amendments to the claims under PCT Article 19.

9. [X] An (unexecuted) oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)).

10. [] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

Items 11. to 14. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. [] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. [X] A FIRST preliminary amendment.

    [] A SECOND or SUBSEQUENT preliminary amendment.

14. [X] Other items or information: (a) PCT Request; (b) Forms PCT/IB/301, 304 and 308; (c) Norwegian Search Report; (d) International Preliminary Examination Report with amended sheets for claims 1-8 and page 1A of specification; and (e) published International Application (WO 01/02614) with attached Figs. 1-9 (A4 paper) and International Search Report

JC13 Rec'd PCT/PTO 31 DEC 2001

U.S. APPLICATION NO. NEW 10/019431	INTERNATIONAL APPLICATION NO. PCT/NO99/00324	ATTORNEY'S DOCKET NO. 2001_1848A	
15. [X] The following fees are submitted		CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee nor international search fee paid to USPTO and International Search Report not prepared by the EPO or JPO .... $1040.00 International Search Report has been prepared by the EPO or JPO .... $ 890.00 International preliminary examination fee not paid to USPTO but international search paid to USPTO .... $ 740.00 International preliminary examination fee paid to USPTO but claims did not satisfy provisions of PCT Article 33(1)-(4) .... $ 690.00 International preliminary examination fee paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) .... $ 100.00			
ENTER APPROPRIATE BASIC FEE AMOUNT =		$1040.00	
Surcharge of $130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	8 -20 =	0	X $18.00	$	
Independent Claims	2 -3 =	0	X $84.00	$	
Multiple dependent claim(s) (if applicable)			+ $280.00	$	
TOTAL OF ABOVE CALCULATIONS =				$1040.00	
[] Small Entity Status is hereby asserted. Above fees are reduced by 1/2.				$	
SUBTOTAL =				$1040.00	
Processing fee of $130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$1040.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40 per property +				$	
TOTAL FEES ENCLOSED =				$1040.00	
				Amount to be refunded	$
				Amount to be charged	$

a. [X] A check in the amount of $1040.00 to cover the above fees is enclosed. A duplicate copy of this form is enclosed.

b. [] Please charge my Deposit Account No. 23-0975 in the amount of $__________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0975.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

19. CORRESPONDENCE ADDRESS

000513

PATENT TRADEMARK OFFICE

By: Michael R. Davis

Michael R. Davis,
Registration No. 25,134

WENDEROTH, LIND & PONACK, L.L.P.
2033 "K" Street, N.W., Suite 800
Washington, D.C. 20006-1021
Phone:(202) 721-8200
Fax:(202) 721-8250

December 31, 2001

THE COMMISSIONER IS AUTHORIZED TO CHARGE ANY DEFICIENCY IN THE FEES FOR THIS PAPER TO DEPOSIT ACCOUNT NO. 23-0975

[CHECK NO. 48189]

[2001_1848A]

#4/a

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :

Ketil PETTERSEN et al. : **Attn: BOX PCT**

Serial No. NEW : **Docket No. 2001_1848A**

Filed December 31, 2001 :

CORROSION RESISTANT Mg BASED
ALLOY CONTAINING Al, Si, Mn and
RE METALS
**[Corresponding to PCT/NO99/00324
Filed October 25, 1999]**

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents,
Washington, DC 20231

Sir:

Please amend the above-identified application as follows:

IN THE SPECIFICATION

Page 1, after the title of the invention, please insert:

This application is a 371 application of PCT/NO99/00324 filed October 25, 1999.

IN THE CLAIMS

Cancel, without prejudice to the subject matter involved, claims 1-9.

Please add new claims 10-17 as follows:

10. (New) A magnesium based alloy with improved corrosion resistance, containing 1.5-5 weight % Al, 0.6-1.4 weight % Si, 0.01-0.6 weight % Mn, 0.01-0.4 weight % RE, up to 0.5 weight % Zn, the balance being Mg and impurities.

11. (New) The magnesium alloy according to claim 10, wherein the Zn content is in the range 0.1-0.3 weight %.

12. (New) The magnesium alloy according to claim 10, wherein the Mn content is in the range 0.01-0.3 weight %.

13. (New) The magnesium alloy according to claim 10, wherein the rare earth elements are Misch metal.

14. (New) The magnesium alloy according to claim 10, containing 1.9-2.5 weight % Al, 0.7-1.2 weight % Si, 0.15-0.25 weight % Zn, 0.01-0.3 weight % RE and 0.01-0.2 weight % Mn, the balance being Mg and impurities.

15. (New) A method of improving the corrosion resistance of magnesium-aluminium-silicon alloys, where Mn is added in order to reduce Fe impurities, by keeping both Mn and Fe at a low level by adding small amounts of RE.

16. (New) The method according to claim 15, wherein the Mn content is kept above 0.01 weight %.

17. (New) The method according to claim 15, wherein the RE content is kept in the range 0.01-0.4 weight %.

REMARKS

The specification has been amended to insert a cross-reference to the international application.

Original claims 1-9 have been canceled in favor of new claims 10-17, which correspond to claims 1-8, respectively, attached to the International Preliminary Examination Report.

Respectfully submitted,

Ketil PETTERSEN et al.

By Michael R. Davis
Michael R. Davis
Registration No. 25,134
Attorney for Applicants

MRD/aeh
Washington, D.C. 20006-1021
Telephone (202) 721-8200
Facsimile (202) 721-8250
December 31, 2001

CORROSION RESISTANT Mg BASED ALLOY CONTAINING Al, Si, Mn AND RE METALS

Such alloys are used for die casting of for example automotive, transmission and engine parts. Therefore the alloy needs to have good mechanical properties also at elevated temperatures. Alloys for this use available on the market today include AS21, AS41 and AE42. The alloy AS21 has the following composition (Hydro Magnesium Specifications), 1.9-2.5 weight % Al, minimum 0.2 weight % Mn, 0.15-0.25 weight % Zn, 0.7-1.2 weight % Si, maximum 0.008 weight % Cu, maximum 0.001 weight % Ni, maximum 0.004 weight % Fe and maximum 0.01 weight % of other elements each. The alloy AS41B (ASTM B93-94a) contains 3.7-4.8 weight % Al, 0.35-0.6 weight % Mn, maximum 0.10 weight % Zn, maximum 0.60-1.4 weight % Si, maximum 0.015 weight % Cu, maximum 0.001 weight % Ni, maximum 0.0035 weight % Fe and maximum 0.01 weight % of other elements each. The alloy AE42 (Hydro Magnesium Specifications) contains 3.6-4.4 weight % Al, minimum 0.1 weight % Mn, maximum 0.20 weight % Zn, maximum 0.04 weight % Cu, maximum 0.001 weight % Ni, maximum 0,004 weight % Fe, 2.0-3.0 weight % RE and maximum 0.01 weight % of others each. RE refers to rare earth elements. All these alloys contain some iron and as iron is detrimental to the corrosion properties of magnesium aluminium alloys, manganese is used to control and reduce the iron content in the alloys.

In spite of this, the corrosion resistance of for example AS21 is not sufficient in e.g. automotive use. Car parts are subjected to a harsh environment especially at winter time when de-icing agents are applied to the roads. The alloy AE42 has good corrosion properties also in this environment, but it is more expensive than e.g. AS21. In addition, the casting properties are not as good as for the others, particularly due to a tendency to stick and solder to the die.

Alloys of this type are also described for example in Norwegian patent No. 121 753 , US patent No. 3 718 460 and French patent No. 1 555 251.

The object of the invention is to improve the corrosion resistance without detoriation of basic properties of magnesium-aluminium-silicon alloys. Another object is to avoid increased costs of the alloy.

These and other objects of the invention are obtained by the alloy as described below. The invention is further described and characterized by the accompanying patent claims.

The invention concerns a magnesium based alloy with improved corrosion resistance, containing 1.5-5 weight % Al, 0.6-1.4 weight % Si, 0.01-0.6 weight % Mn, 0.01-0.4 weight % RE. The content of impurities should be kept at a low level with maximum 0.008 weight % Cu, maximum 0.001 weight % Ni, maximum 0.004 weight % Fe and maximum 0.01 weight % of other elements each. Particularly, a Mn content of 0.05 - 0.2 weight % is favorable. In addition, it is preferable to add until 0.5 weight % Zn and especially 0.1- 0.3 weight % Zn. This element has a positive effect on corrosion resistance. The rare earth elements used are preferably in the form of Misch metal. A preferred alloy contains 1.9-2.5 weight % Al, 0.7-1.2 weight % Si, 0.15-0.25 weight % Zn, 0.01-0.3 weight % RE and 0.01-0.2 weight % Mn. The invention also concerns a method of improving the corrosion resistance of magnesium, aluminium, silicon alloys where Mn is added in order to reduce Fe impurities, by keeping both Mn and Fe at a low level by adding small amounts of RE. It is preferred to keep the Mn content above 0.01 weight % and the RE content in the range 0.01-0.4.

The invention will be further illustrated with reference to Figures 1-9, where

Figure 1 shows the combination of Mn and RE content found in the the investigated specimens. These compositions span the temperature range from 650 °C - 720 °C. The mutually limited solubility of Mn and RE restricts the investigation to the lower left half of the figure.

Figure 2 shows the Fe content in the specimens analyzed in the test program.

Figure 3 shows corrosion rates (MCD = mg/cm²day) of immersion tested of gravity cast disc samples versus RE and Mn content of the investigated specimens.

Figure 4 shows corrosion rates versus Mn and Fe content of the investigated specimens. The results are from 72 hours immersion tests of gravity cast disc samples.

Figure 5 shows corrosion rates versus RE content and casting temperature for the gravity cast disc samples containing minimum 0.045 weight% Mn.

Figure 6 shows corrosion rates versus Mn and RE content of the investigated die cast plates. In this investigation the Mn and the RE contents were varied in the range 0.05 - 0.35 weight%.

Figure 7 shows corrosion rates for the die cast plates, tested in salt spray for 240 hours according to ASTM B117, versus Mn and Fe content. The trends as observed in the immersion tests of the gravity cast disc samples are also found here.

Figure 8 shows the individual corrosion test results versus Al-content for two series of alloys.

Figure 9 shows mean values of corrosion test results versus Al-content for two series of alloys when the outliers are excluded.

The present findings show that it is possible to significantly improve the corrosion resistance of magnesium alloys with aluminium and silicon by the addition of small amounts of Rare Earth (RE) elements. One or more of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium may be used as rare earth elements. However, it is expensive to isolate the individual rare earth elements, so Misch metal, which is comparatively cheap, may preferably be used.

In Mg-Al-Si based alloys the solubilities of Mn, RE and Fe are mutually restricted. In addition, reduced temperature reduces their mutual solubility.

Several experiments have been carried out and are described in the following examples.

Example 1

Magnesium alloys of the type AS21 have been prepared with different combinations of Mn and RE. Table 1 and Figure 1 shows the different combinations of Mn and RE which are investigated. The Rare Earth elements are added in the form of Misch metal, a mixture of Ce, La Pr and Nd (Approx. 55 weight % Ce, 25 weight %La, 15 weight % Nd, 5 weight % Pr). Other mixtures of Rare Earth elements are expected to give the same effect.

The other elements Al, Si and Zn were held constant within the specification of the alloy, and close to 2.2 %, 1.0 % and 0.2 % respectively. The alloys were prepared by adding controlled amounts of Mn and RE to the alloy at temperatures around 740 °C (for some compositions about 760 °C), and then giving the alloys time to stabilize at specified temperatures before casting of test samples for chemical analysis and corrosion tests. The Fe content of the specimens is a result of the equilibrium condition established.

In addition, unmodified AS21 was also tested and the results are included in Table 1.

The corrosion resistance was determined for gravity cast disc samples by immersing into a solution of 5 % NaCl at 25 °C for 72 hours. The ratio between test solution and sample surface was 10 ml/cm^2 in all the tests. The casting temperature and corrosion rate for gravity cast disc samples are included in Table 1. The corrosion rates are determined by weight loss measurements and are measured in MCD (mg/cm^{2}day).

Table 1. *Casting temperature, composition and corrosion rates for the permanent mold cast medallions included in this investigation.*

Temp. [°C]	Al [weight%]	Zn [weight%]	Mn [weight%]	Si [weight%]	Fe [ppm]	RE [weight%]	Corrosion rate [MCD]
650	2,42	0,19	0,00	0,96	12	0,10	4,9
650	2,18	0,19	0,16	0,99	21	0,00	4,2
650	2,44	0,20	0,03	0,98	6	0,11	1,3
650	2,46	0,20	0,05	0,95	2	0,11	1,6
650	2,40	0,19	0,01	0,99	9	0,09	3,4
660	2,30	0,16	0,24	0,88	4	0,00	4,4
660	2,30	0,17	0,24	1,00	9	0,00	4,0
660	2,40	0,18	0,25	0,91	6	0,00	4,6
660	2,07	0,20	0,06	0,99	4	0,12	1,1

660	2,30	0,18	0,22	0,99	8	0,00	3,9
660	2,30	0,18	0,18	0,94	18	0,00	4,7
660	2,20	0,17	0,17	1,02	27	0,00	4,3
660	2,20	0,17	0,06	0,99	53	0,00	5,5
660	2,18	0,21	0,04	1,01	6	0,13	0,6
660	2,40	0,17	0,00	1,01	75	0,00	88,0
660	2,23	0,21	0,22	1,00	10	0,01	4,4
660	2,26	0,21	0,25	0,86	10	0,01	4,7
660	2,15	0,20	0,12	0,98	5	0,04	2,3
680	2,04	0,20	0,07	0,96	4	0,14	1,0
680	2,30	0,17	0,20	0,96	45	0,00	6,9
680	2,39	0,19	0,01	0,95	14	0,18	5,0
680	2,30	0,18	0,26	1,00	18	0,00	5,4
680	2,48	0,20	0,07	0,98	5	0,17	2,1
680	2,30	0,16	0,31	0,90	6	0,00	5,4
680	2,30	0,17	0,29	0,97	9	0,00	4,7
680	2,40	0,18	0.31	0,90	5	0,00	5,2
680	2,48	0,20	0,01	1,03	16	0,16	6,9
680	2,20	0,17	0,18	1,01	49	0,00	6,4
680	2,30	0,21	0,29	0,87	20	0,01	5,9
680	2,21	0,20	0,20	1,02	52	0,00	6,3
680	2,40	0,18	0,00	1,03	96	0,00	97,3
680	2,23	0,21	0,05	1,01	10	0,16	0,8
680	2,20	0,17	0,06	0,97	73	0,00	8,1
680	2,18	0,21	0,13	1,00	7	0,05	2,0
680	2,45	0,20	0,04	0,99	10	0,18	3,0
680	2,16	0,21	0,24	0,98	22	0,02	5,3
700	2,30	0,17	0,21	0,96	82	0,00	9,4
700	2,28	0,21	0,31	0,87	39	0,02	8,5
700	2,13	0,20	0,10	1,00	5	0,17	1,0
700	2,30	0,17	0,28	1,01	39	0,00	7,3
700	2,22	0,21	0,26	1,01	24	0,03	5,4
700	2,40	0,17	0,00	1,02	113	0,00	93,4
700	2,20	0,17	0,18	1,02	73	0,00	7,8
700	2,20	0,17	0,07	0,98	97	0,00	11,2
700	2,40	0,17	0,36	0,96	6	0,00	6,1
700	2,25	0,21	0,05	1,02	15	0,23	2,2
700	2,23	0,21	0,15	1,01	10	0,08	2,0
700	2,30	0,18	0,39	0,94	8	0,00	6,7
700	2,40	0,15	0,37	0,94	13	0,00	7,4
710	2,21	0,20	0,21	1,03	111	0,00	10,2
710	2,48	0,20	0,04	1,01	25	0,21	6,3
710	2,47	0,20	0,01	1,03	30	0,20	14,6
710	2,46	0,19	0,01	1,01	25	0,28	7,6
710	2,50	0,20	0,08	0,99	20	0,20	3,7
720	2,20	0,17	0,18	1,01	110	0,00	9,7
720	2,30	0,16	0,42	1,01	18	0,00	9,3
720	2,30	0,17	0,00	0,99	149	0,00	95,6

720	2,20	0,17	0,07	0,97	134	0,00	16,4
720	2,22	0,21	0,15	1,01	23	0,11	1,9
720	2,40	0,15	0,42	0,96	29	0,00	10,2
720	2,25	0,21	0,33	0,86	113	0,02	12,0
720	2,30	0,17	0,29	1,00	77	0,00	12,4
720	2,40	0,18	0,44	0,93	15	0,00	10,5
720	2,28	0,21	0,05	1,04	23	0,30	3,3
720	2,24	0,21	0,11	1,03	23	0,19	1,5
720	2,26	0,21	0,27	1,01	40	0,04	6,9
720	2,30	0,17	0,21	0,93	121	0,00	13,0
740	2,30	0,17	0,44	0,97	40	0,00	13,9
740	2,30	0,17	0,21	0,94	155	0,00	18,9
740	2,20	0,16	0,06	0,94	181	0,00	24,5
740	2,30	0,17	0,30	1,13	122	0,00	16,9
740	2,30	0,17	0,18	1,00	135	0,00	13,0
740	2,30	0,17	0,00	0,99	189	0,00	69,1
760	2,30	0,17	0,18	1,00	189	0,00	19,6
760	2,40	0,17	0,00	1,01	243	0,00	60,8
760	2,30	0,17	0,06	0,97	246	0,00	26,4
760	2,30	0,17	0,22	0,93	219	0,00	22,2
760	2,30	0,17	0,30	1,01	150	0,00	19,8

The corresponding Fe contents are shown in Figure 2. The figure includes data from different temperatures. It illustrates that all specimens containing more than 0.05 weight % RE have a Fe content below 40 ppm, while the specimens without RE may contain higher levels of Fe.

The corrosion rates are also given in Tables 1 and 2. The corrosion rates are illustrated vs. Mn and RE contents in Figure 3. The corrosion rate is at a minimum for compositions with a Mn content between 0.05 and 0.2 weight %, and a RE content above 0.05 weight %. Comparing Figures 2 and 3 reveals that there is no direct correlation between the Fe content and the corrosion rates, also the content of Mn and RE has a significant influence.

This can be seen in Figure 4, where the corrosion rates are plotted vs. the content of Mn and Fe, and the minimum is reached when both elements are at a low level. This is, however, not possible to obtain without the addition of other alloying elements, like the RE elements. Furthermore, the corrosion rates increase when the Mn content is below 0.05 weight%. Thus, the presence of a low level of Mn is necessary for an optimum effect.

The effect of RE addition of increased temperature is unexpected. Figure 5 presents corrosion rates vs. RE content and casting temperature for the gravity cast disc samples containing a minimum of 0.045 weight% Mn. Due to the increased solubility of Mn and Fe with increased temperature, increased temperature has a strong negative effect on the corrosion resistance of unmodified AS21. With the addition of RE elements, the equilibrium levels of Mn and Fe are strongly reduced also at higher temperatures, thereby significantly reducing the corrosion rates.

Example 2

The alloy AS21 is produced for application as a die casting alloy. A selected set of compositions, as shown in Table 2, was therefore die cast into test plates, and tested in salt-spray according to ASTM standard no. B117-90. The corrosion results are included in Table 2 and are shown in Figures 6 and 7. There is correspondence between the corrosion rates determined for die cast plates and gravity cast disc samples. An optimum composition range is found for compositions with 0.05 - 0.2 weight % RE, and 0.05 - 0.2 weight % Mn.

Table 2. *Casting temperature, composition and corrosion rates for the die cast test plates included in this investigation. The corrosion rates are determined after 240 hours exposure in salt-spray.*

Temp. [°C]	Al [weight%]	Zn [weight%]	Mn [weight%]	Si [weight%]	Fe [ppm]	RE [weight%]	Corrosion rate [MCD]
720	2,25	0,21	0,33	0,86	113	0,02	13,6
700	2,28	0,21	0,31	0,87	39	0,02	4,5
680	2,30	0,21	0,29	0,87	20	0,01	1,8
660	2,26	0,21	0,25	0,86	10	0,01	0,3
720	2,26	0,21	0,27	1,01	40	0,04	2,1
700	2,22	0,21	0,26	1,01	24	0,03	1,7
680	2,16	0,21	0,24	0,98	22	0,02	1,1
660	2,23	0,21	0,22	1,00	10	0,01	0,6
720	2,22	0,21	0,15	1,01	23	0,11	0,4
700	2,23	0,21	0,15	1,01	10	0,08	0,2
680	2,18	0,21	0,13	1,00	7	0,05	0,2
660	2,15	0,20	0,12	0,98	5	0,04	0,1
720	2,24	0,21	0,11	1,03	23	0,19	0,7
700	2,13	0,20	0,10	1,00	5	0,17	0,0
680	2,04	0,20	0,07	0,96	4	0,14	0,3
660	2,07	0,20	0,06	0,99	4	0,12	0,1
720	2,28	0,21	0,05	1,04	23	0,30	0,5
700	2,25	0,21	0,05	1,02	15	0,23	0,5

680	2,23	0,21	0,05	1,01	10	0,16	0,2
660	2,18	0,21	0,04	1,01	6	0,13	0,0

In addition to die casting of test plates, large engine parts with casting weights of 20 kg have been cast from the alloy. In comparison with the unmodified AS21, the castability was not significantly affected.

The mechanical properties of the alloys are governed by the content of Al, Si, and Zn, and is not significantly affected by the modification by addition of RE elements.

Example 3

Two melts, each of 150 kg Mg alloy were produced in the foundry lab. Each of the melts were produced with 1.5 % Al, 1.0 % Si and 0.2 % Zn. One melt was produced with 0.4 % added Mn, the other with 0.3 % RE + 0.1 % Mn. The alloys were produced at 740 °C, thereafter stabilised at 680 °C for at least 1 hour before casting of permanent mould cast disc samples and 3 mm die cast test plates. Each melt was further alloyed with super purity Al in steps of 1 % to cover the Al-range given in claim 1. This alloying was done at 680 °C, and the alloys were stabilised for at least 1 hour before further casting. The chemical analysis of each composition is shown in Table 3. The analysis was carried out by spark emission spectrograph, the RE-elements by ICP-AES.

Table 3. *Chemical compositions of the investigated specimens*

Speci-men I.D	Al [wt%]	Zn [wt%]	Mn [wt%]	Si [wt%]	Fe [wt%]	Cu [wt%]	Ni [wt%]	Be [ppm]	Sum RE [wt%]
U-1	1.388	0.201	0.269	0.9334	0.0018	0.0002	0.0002	0.9	0
U-2	2.322	0.208	0.258	0.9108	0.0027	0.0002	0.0002	0.9	0
U-3	3.203	0.205	0.256	0.9065	0.0034	0.0002	0.0002	0.9	0
U-4	4.092	0.207	0.264	0.9143	0.0047	0.0002	0.0002	0.9	0
U-5	4.974	0.205	0.286	0.9248	0.0056	0.0002	0.0002	0.9	0
M-1	1.490	0.202	0.074	0.8880	0.0022	0.0002	0.0002	0.9	0.16
M-2	2.544	0.207	0.071	0.9065	0.0029	0.0002	0.0002	0.9	0.15
M-3	3.463	0.204	0.070	0.8835	0.0041	0.0002	0.0002	0.9	0.16
M-4	4.421	0.206	0.070	0.9103	0.0048	0.0002	0.0002	0.9	0.16
M-5	5.349	0.210	0.087	0.9323	0.0123	0.0002	0.0002	2.8	0.2

Four die cast test plates from each composition were tested in salt-spray for 10 days according to ASTM B117. The results are shown in Table 4, and in Figure 8. For some of the compositions there were single results diverging significantly from the rest of the same series. The average results without the outliers are shown in Figure 9. The outliers are here defined as single results lying more that 4x standard deviation outside the average of the other parallels. These are also marked in Table 4.

Table 4. *Corrosion test results in MCD ($\frac{mg\ weight\ loss}{cm^2\ x\ day}$). Outliers are marked with bold italic*

Speci-men I.D.	MCD	MCD	MCD	MCD	Mean	Std Dev.	Mean ex outlier	Std dev. ex outlier
U-1	1	1.2	1.3	***4.3***	2.0	1.6	1.17	0.12
U-2	0.3	0.4	0.7	***7.8***	2.3	3.7	0.47	0.17
U-3	0.51	0.6	0.7	***2.4***	1.1	0.9	0.60	0.08
U-4	0.32	0.38	0.42	***0.9***	0.5	0.3	0.37	0.04
U-5	0.24	0.31	0.31	0.33	0.3	0.04	0.30	0.03
M-1	0.07	0.07	0.08	0.09	0.08	0.01	0.08	0.01
M-2	0.05	0.05	0.09	***0.26***	0.11	0.1	0.06	0.02
M-3	0.03	0.03	0.04	0.06	0.04	0.01	0.04	0.01
M-4	0.03	0.04	0.04	0.05	0.04	0.01	0.04	0.01
M-5	0.04	0.06	0.06	***0.21***	0.09	0.08	0.05	0.01

The compositions of the two series are very similar, except for the Mn and the RE content. Even though super purity Al was used, the Fe-content is increasing together with the Al-addition. This Fe-pick up was fairly similar for the two series, except at the highest Al-level, where the RE-modified alloy reached 123 ppm Fe, compared to 56 ppm in the unmodified.. For the series without RE, the corrosion rates decreases with increasing Al, in spite of the increasing Fe. For the series modified with RE, the corrosion rates are significantly lower, and no obvious trends with variation of Al and Fe can be seen. The results clearly show that the corrosion rates of the RE-modified alloy is significantly lower than for the unmodified alloy through the whole Al-composition range. For several compositions there are outliers with significantly higher corrosion rates than the other specimens from the same series. The background for these high individual results are not investigated. These outliers are not influencing on the conclusion of this investigation.Thus, the modification of AS-alloys by substituting some of the Mn with

RE-elements has a significant positive effect on the corrosion resistance over the whole composition range of 1.5 - 5 % Al.

The corrosion resistance of magnesium-aluminium-silicon based alloys is significantly improved by the addition of RE elements by:

1) Reducing the solubility of Mn

2) Reducing the solubility of Fe

3) Modifying the corrosion behavior by the presence of RE. The presence of small amounts of Mn (above 0.01 weight %) is necessary for an optimum effect of the modification.

This positive effect of RE elements on corrosion resistance will also apply for other levels of Si and Zn in the AS-alloys.

Patent claims

1. Magnesium based alloy with improved corrosion resistance, containing 1.5-5 weight % Al, 0.6-1.4 weight % Si, 0.01-0.6 weight % Mn, 0.01-0.4 weight % RE.

2. Magnesium alloy according to claim 1, wherein the alloy contains until 0.5 weight % Zn.

3. Magnesium alloy according to claim 2, wherein the Zn content is in the range 0.1-0.3 weight %.

4. Magnesium alloy according to claim 1, wherein the Mn content is in the range 0.01-0.3 weight %.

5. Magnesium alloy according to claim 1, wherein the rare earth elements are Misch metal.

6. Magnesium alloy according to claim 1 - 2, comprising 1.9-2.5 weight % Al, 0.7-1.2 weight % Si, 0.15-0.25 weight % Zn, 0.01-0.3 weight % RE and 0.01-0.2 weight % Mn.

7. Method of improving the corrosion resistance of magnesium, aluminium, silicon alloys where Mn is added in order to reduce Fe impurities, by keeping both Mn and Fe at a low level by adding small amounts of RE.

8. Method according to claim 7, where the Mn content is kept above 0.01 weight %.

9. Method according to claim 7, wherein the RE content is kept in the range 0.01-0.4 weight %.

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(71) Applicant *(for all designated States except US)*: **NORSK HYDRO ASA** [NO/NO]; N-0240 Olso (NO).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **PETTERSEN, Ketil** [NO/NO]; Gråsteinveien 14, N-3931 Porsgrunn (NO). **VIDEM, Marianne** [NO/NO]; Tømmerveien 54, N-3943 Porsgrunn (NO). **SKAR, Jan, Ivar** [NO/NO]; Lærer Johnsens vei 2, N-3960 Stathelle (NO).

(74) Agent: ANDERSON, Elin; Norsk Hydro ASA, N-0240 Oslo (NO).

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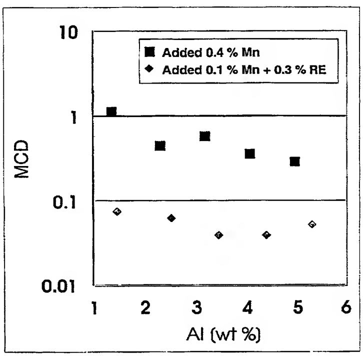
(54) Title: CORROSION RESISTANT Mg BASED ALLOY CONTAINING Al, Si, Mn AND RE METALS



(57) Abstract: Magnesium alloy with improved corrosion resistance comprising magnesium, 1.5-5 weight % Al, 0.6-1.4 weight % Si, 0.01-0.6 weight % Mn and 0.01-0.4 weight % RE. Method of improving the corrosion resistance of magnesium, aluminium, silicon alloys where Mn is added in order to reduce FE impurities, by keeping both Mn and Fe at a low level by adding small amounts of RE.

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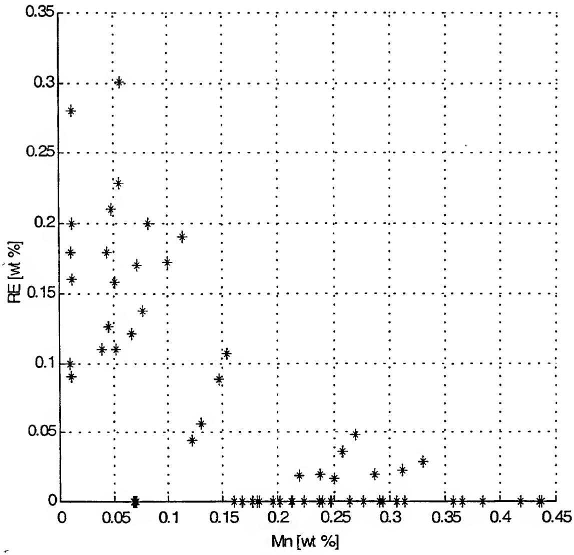
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
RE [wt %]
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
Mn [wt %]

FIG. 1

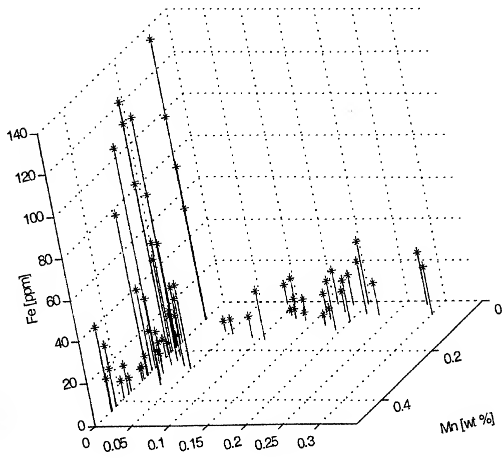
140
120
100
80
60
40
20
0
Fe [ppm]
0
0.05
0.1
0.15
0.2
0.25
0.3
RE [wt %]
0
0.2
0.4
Mn [wt %]

FIG.2

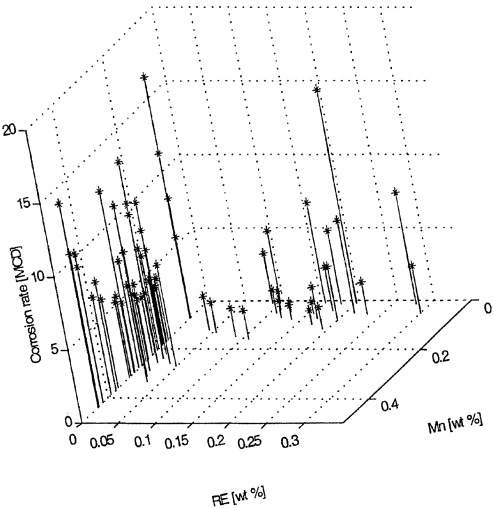
Corrosion rate [MCD]
20
15
10
5
0
0
0.05
0.1
0.15
0.2
0.25
0.3
RE [wt %]
0
0.2
0.4
Mn [wt %]

FIG. 3

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PCT/NO99/00324

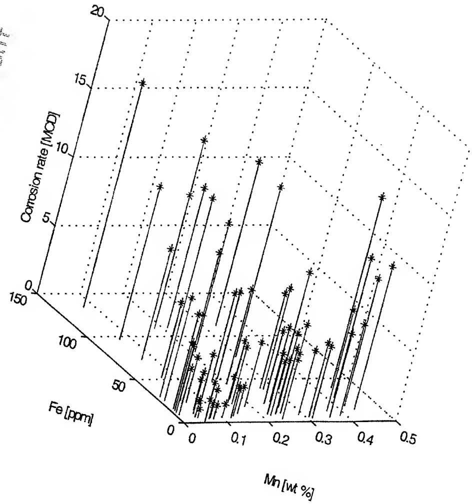

FIG. 4

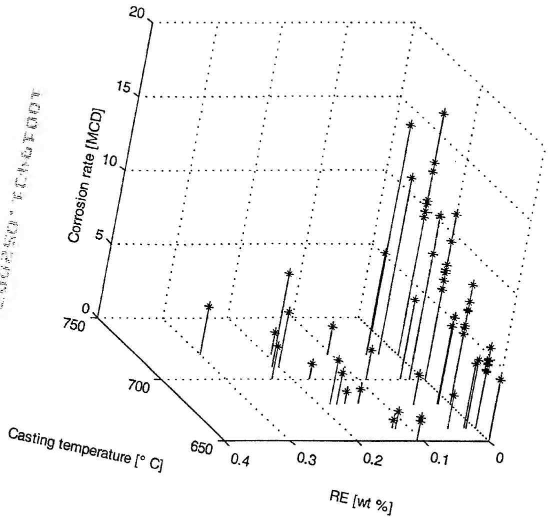
20
15
10
5
0
Corrosion rate [MCD]
750
700
650
Casting temperature [° C]
0.4
0.3
0.2
0.1
0
RE [wt %]

FIG. 5

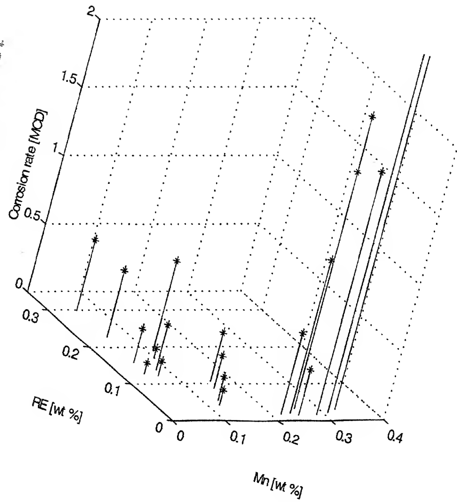

FIG. 6

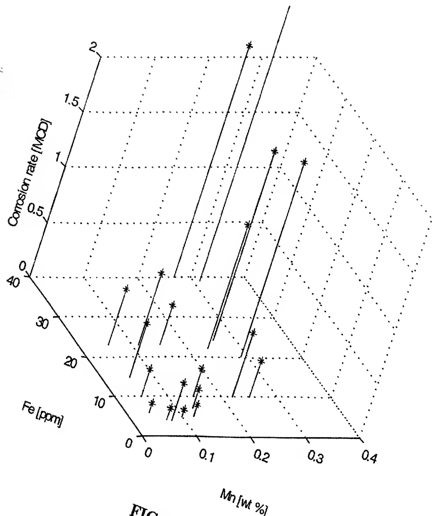
Corrosion rate [MOD]
2
1.5
1
0.5
0
40
30
20
10
0
Fe [ppm]
0
0.1
0.2
0.3
0.4
Mn [wt %]

FIG. 7

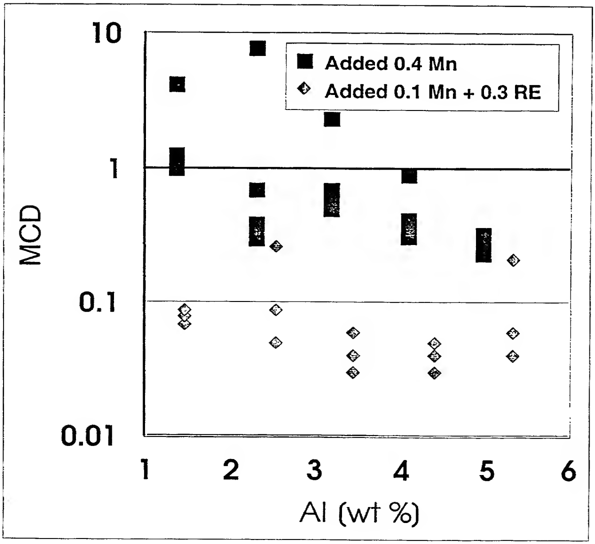

FIG. 8

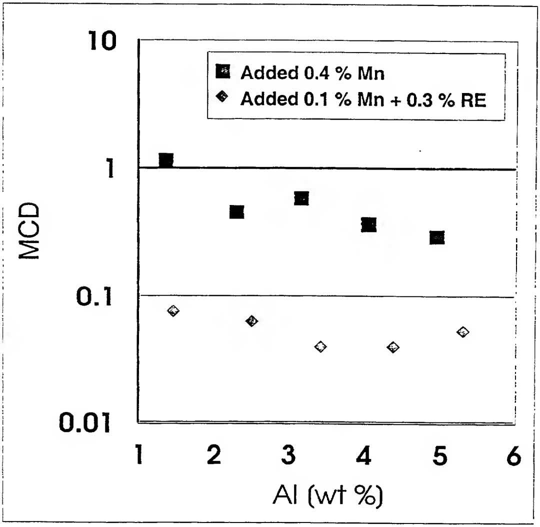

FIG. 9

P9945 US

Rev. 3-21-01

Effective March 1998

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

() Original () Supplemental () Substitute (X) PCT () DESIGN

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Title: CORROSION RESISTANT Mg BASED ALLOY CONTAINING Al, Si, Mn and RE METALS

of which is described and claimed in:
() the attached specification, or
() the specification in application Serial No. , filed , and with amendments through __________, or
(X) the specification in International Application No. PCT/NO99/00324, filed October 25, 1999, and as amended on July 4, 2001 (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
Norway	19993289	July 2, 1999	yes

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

And I hereby appoint Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Warren M. Cheek, Jr., Reg. No. 33,367; Nils Pedersen, Reg. No. 33,145; Charles R. Watts, Reg. No. 33,142; and Michael S. Huppert, Reg. No. 40,268, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., as well as any other attorneys and agents associated with Customer No. 000513, to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys and agents named herein to accept and follow instructions from NORSK HYDRO ASA as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

Direct Correspondence to Customer No:	Direct Telephone Calls to:
000513 PATENT TRADEMARK OFFICE	WENDEROTH, LIND & PONACK, L.L.P. 2033 "K" Street, N.W., Suite 800 Washington, D.C. 20006-1021 Phone:(202) 721-8200 Fax:(202) 721-8250

-00

Full Name of First Inventor	FAMILY NAME PETTERSEN	FIRST GIVEN NAME Ketil	SECOND GIVEN NAME	
Residence & Citizenship	CITY Porsgrunn	STATE OR COUNTRY Norway NOX	COUNTRY OF CITIZENSHIP Norway	
Post Office Address	ADDRESS Gråsteinveien 14, N-3931 Porsgrunn, Norway	CITY	STATE OR COUNTRY	ZIP CODE

2-00

Full Name of Second Inventor	FAMILY NAME VIDEM	FIRST GIVEN NAME Marianne	SECOND GIVEN NAME	
Residence & Citizenship	CITY Porsgrunn	STATE OR COUNTRY Norway NOX	COUNTRY OF CITIZENSHIP Norway	
Post Office Address	ADDRESS Tømmerveien 54, N-3943 Porsgrunn, Norway	CITY	STATE OR COUNTRY	ZIP CODE

3-00

Full Name of Third Inventor	FAMILY NAME SKAR	FIRST GIVEN NAME Jan	SECOND GIVEN NAME Ivar	
Residence & Citizenship	CITY Stathelle	STATE OR COUNTRY Norway NOX	COUNTRY OF CITIZENSHIP Norway	
Post Office Address	ADDRESS Lærer Johnsens vei 2, N-3960 Stathelle, Norway	CITY	STATE OR COUNTRY	ZIP CODE

Full Name of Fourth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP	
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY	ZIP CODE

Full Name of Fifth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP	
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY	ZIP CODE

Full Name of Sixth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP	
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY	ZIP CODE

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor X Ketil Pettersen — Ketil PETTERSEN — Date X 19/2 - 2002

2nd Inventor X Marianne Videm — Marianne VIDEM — Date X 19/2 - 2002

3rd Inventor X Jan Ivar Skar — Jan Ivar SKAR — Date X 11/3 · 2002

4th Inventor ______ Date ______

5th Inventor ______ Date ______

6th Inventor ______ Date ______

The above application may be more particularly identified as follows:

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Applicant Reference Number P9945 EAn:ELS Atty Docket No. 2001_1848A

Title of Invention CORROSION RESISTANT Mg BASED ALLOY CONTAINING Al, Si, Mn and RE METALS